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Salt separation and purification concepts in integrated farm drainage management systems

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Abstract. *Agriculture on the west side of the San Joaquin Valley of California, like many irrigated arid land agricultures, suffers from increasing soil salinity and water logging and faces large scale land retirement in the near future if salts and subsurface drainage cannot be removed. Following discovery of avian deformities and mortalities at Kesterson reservoir due to high selenium levels, closure of drains originally intended to convey subsurface drainage out of the Valley left farmers with few alternatives. Integrated farm drainage management (IFDM) systems employing sequential water reuse have emerged in recent years as potential phytoremediation techniques to improve salinity management. Development of acceptable final salt removal approaches is critical to the overall success of such systems. Solubility characteristics of sodium sulfate offer the potential to recover purified sulfate for commercial markets. Salt separation and purification using solar concentration and ambient cooling processes are currently being analyzed and tested. Sodium sulfate recoveries depend on the composition of the drainage feed to the concentrator along with local meteorological conditions and may range from as low as 28% to more than 85% of total salt.*

Keywords. *Agricultural subsurface drainage water, salinity, salt, sodium sulfate, chloride, solar evaporation, concentration, separation, recovery, purification, markets*

Salt separation and purification concepts in integrated farm drainage management systems

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Introduction

The San Joaquin Valley of California is currently one of the top producing agricultural areas in the world, growing a wide range of high value commodities (CERES, 2003). The valley, like much of the state, is a semi-annual desert, receiving virtually no precipitation during the months of May through September and only 125 to 250 mm of rainfall annually. What precipitation does occur contributes little to direct recharge of groundwater. The valley agricultural system was transformed during the twentieth century by the construction of aqueducts delivering water from other regions of the state to supplement ground water irrigation sources that were heavily overdrawn and with overdraft contributing to rapid ground subsidence.

Initial plans for irrigating the valley acknowledged the need for salt management. Although imported water quality was good, the large volumes of water to be delivered meant that a large quantity of salt would also be imported and distributed across agricultural lands. Fertilization would add salts, and irrigation would solubilize native salts, further increasing salt concentrations in soil and shallow groundwater unless adequate means of removal were provided. Without proper salt management, irrigation of the valley would prove unsustainable, eventually leading to abandonment of farming in the region as has happened historically in most cases of irrigated arid land agriculture.

The San Joaquin Valley is composed of two geologic basins, the upper San Joaquin basin drained by the San Joaquin River flowing northwards to the Sacramento-San Joaquin River Delta, and the hydrologically closed Tulare Lake Hydrologic Basin (also referred to as the Tulare Basin) making up the southern half of the valley (USDOI/CRA, 1990). The western valley is divided into three major hydrogeologic zones (Figure 1): 1) an upper semi- to un-confined aquifer, 2) a confining clay layer (the Corcoran clay), and 3) a confined aquifer below the clay (SJVDIP, 2000). The upper semi-confined zone is comprised largely of three other hydrogeologic units including a Coast range alluvium extending from the western Coast mountain range towards the center of the valley and running over a Sierran sand deposit extending from the east. Flood basin deposits from the San Joaquin River are located in the valley trough. The Corcoran clay layer is an inhomogeneous zone of multiple clay layers interbedded with more permeable materials. The confined layer below is comprised principally of flood basin, deltaic, lacustrine, and alluvial deposits. The Tulare Lake basin is characterized by dry or ephemeral lakebeds and lake sediments in addition to the three hydrogeologic subunits of the semi-confined zone found throughout the valley. Marine Coast range sediments contain salts and various trace elements including selenium, boron, molybdenum, and arsenic. Irrigation

dissolves these into shallow groundwater and drainage water flows. Concentrations are much lower in the Sierran sediments to the east.

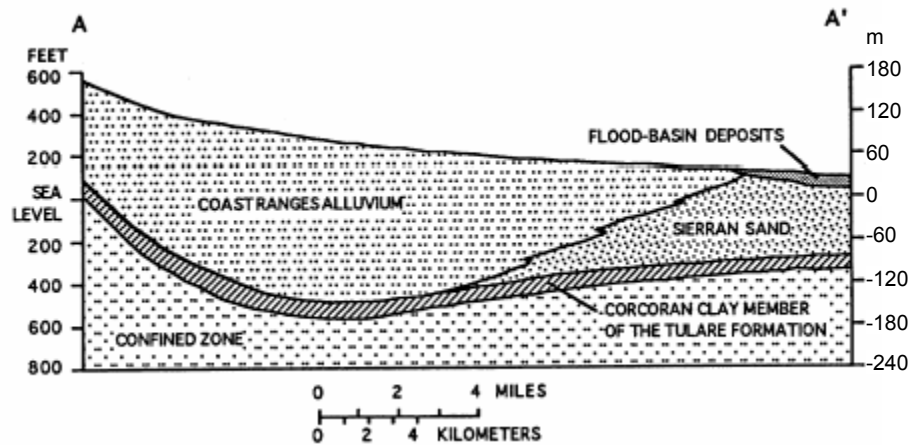


Figure 1. Cross-section through the western San Joaquin Valley of California illustrating the three major hydrogeologic zones (SJVDIP, 2000).

Groundwater recharge on the western side of the valley is primarily via percolation of irrigation water supplied partly from the Sacramento and Feather River surface water systems to the north through the Delta, and partly from groundwater pumping. Average regional irrigation application rates are 0.5 to 0.7 m of water. Seepage from rivers, streams, and unlined canals also contributes to groundwater recharge.

Following construction of aqueducts delivering surface water for irrigation as part of the Central Valley Project (CVP) and State Water Project (SWP), groundwater pumping rates in the valley declined and water tables began to rise. The upper semi-confined zone has saturated in much of the western valley. Most groundwater pumping is now from the confined zone below the Corcoran clay. Groundwater is also pumped from the upper zone, but that from the Coast range alluvium is of poor quality in comparison with water obtained from the thicker zones of the Sierran sand. Pumping and drainage from the upper zone is balanced by irrigation recharge. Water pumped from the confined zone is recharged by leakage through the clay from the upper zone and subsurface inflow from the east.

The CVP began delivering water to the northern San Joaquin valley in 1951, irrigating approximately 250,000 ha of farm land. The southern part of the valley began receiving irrigation water from the CVP and the SWP in 1968 to irrigate an additional 400,000 ha. As part of the CVP authorization, construction of an interceptor drain was mandated to transport irrigation drainage water to the Delta for disposal. A southern section of the drain was constructed by 1975, terminating in Kesterson reservoir near Los Banos that had been added to the design with the intent of regulating drainage discharge to the Delta. Kesterson reservoir was designated a national wildlife refuge in 1970. Environmental concerns over water quality impacts on the Delta precluded completion of the final segment of the drain, leaving Kesterson as the drain terminus to store and evaporate

drainage water, a result that concentrated salts and other substances in the reservoir. Discovery of aquatic bird deformities and mortalities associated with toxic selenium concentrations at Kesterson in 1983 led the Secretary of the Interior in 1985 to halt drainage discharge to the reservoir. Feeder drains were plugged in 1986 and the reservoir was closed. Similar contamination has been identified in the Tulare Lake basin and elsewhere, and evaporation ponds otherwise used to dispose of agricultural drainage water are now heavily restricted.

The western valley includes about 1 million ha of irrigable farm land. About 40% of the area is currently impacted by high water tables (within 2 m of the surface), drainage restrictions, and salt accumulation. In the absence of an out-of-valley drainage disposal alternative and given the adverse environmental impacts of drainage disposal in evaporation ponds and rivers, farmers and the state have attempted to identify on-farm or regional solutions for managing groundwater, drainage water, and salt. One alternative developed over the last two decades involves sequential reuse of water on crops of increasing salt tolerance. This integrated on-farm drainage management (IFDM) system has evolved from an agroforestry based phytoremediation concept to a combined approach utilizing multiple stages of plant growth followed by a final physical salt removal step (Cervinka, et al., 1999). The IFDM system (Figure 2) has been implemented in various forms at several sites in the valley and has apparently been effective in avoiding toxic accumulations of salt in the root zones of the main production areas and even in improving soil quality on previously salt affected lands (Cervinka, et al., 1999; 2001). The reuse of drainage water in the system is intended to reduce the total volume of water requiring final disposal or processing. The system relies on well designed drainage systems to collect water percolating below the root zone. It is vulnerable to deep percolation and water migrating from other areas. Crop selection depends on local salinity and concentrations of boron and other elements.

A critical component of the IFDM system and for related on-farm drainage management systems is the final salt removal step. Historically evaporation ponds have been used to evaporate water and concentrate salts. Due to avian wildlife toxicity, evaporation ponds are restricted by regulation and improved means of concentrating and separating salts are sought. Solar evaporators, shallow basins that are irrigated on a frequent basis at rates equal to or less than the daily evaporation rate so as to avoid continuous ponding of water attractive to birds, have been employed for the purposes of recovering salts and are also regulated under California law (California Health and Safety Code Section 25209.10-25209.17). Reverse-osmosis and other separation systems have also been tested, mostly with limited success to date. The cost of salt removal has an important bearing on the overall economic feasibility of IFDM systems. Economic improvements potentially arise from two primary attributes of salt recovery systems. Although mixed salts are present in drainage water, in most cases compositions are dominated by sodium sulfate and sodium chloride and processes are available to separate purified salt products (e.g. Na_2SO_4) for commercial markets, thereby generating revenues from sale of product. Secondly, if evaporation or water removal rates can be increased beyond normal evapotranspiration rates (ET_o), the size of the salt concentration and separation system can be reduced relative to evaporation ponds and solar evaporators. The potential cost benefits depend

on the costs of land relative to the capital and operating costs of an enhanced water removal system.

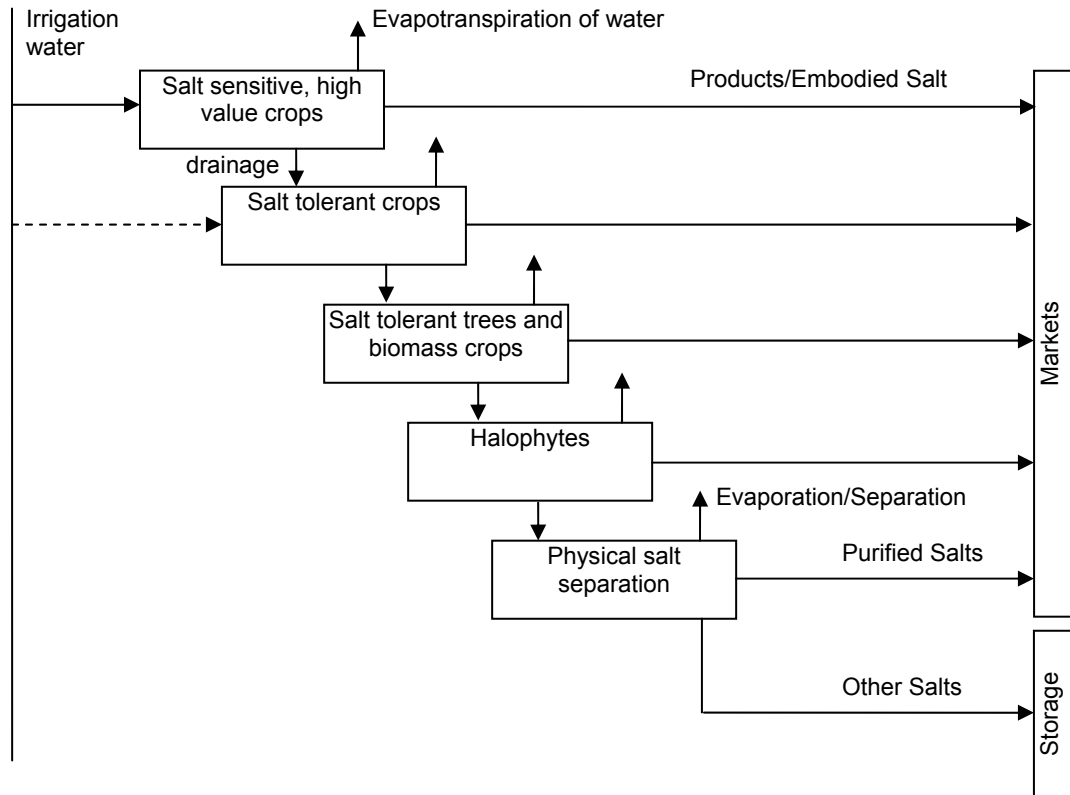


Figure 2. Integrated on-farm drainage management (IFDM) system with sequential reuse of drainage water (after Cervinka, 2001.).

Salt sources and compositions

Annual increases in dissolved salts within the agricultural areas of the western valley are estimated in excess of 5 Tg (SJVDIP, 2000). The principal sources of salt are listed in Table 1, with salt imported in irrigation water, groundwater pumping, and native salt solubilization making up the majority. Salinity in imported irrigation water averages 350 - 400 ppm total dissolved solids (TDS), and firm water supply amounts to 4.2 km³ (USDOI/CRA, 1990).

Table 1. Sources of salt in the western San Joaquin Valley (SJVDIP, 2000).

Source	Quantity of Salt (Tg y ⁻¹)
Imported through Delta	1.60
Groundwater pumping	0.88
Local stream diversion	0.27
Lateral stream inflow	0.14
Canal losses and precipitation	0.09
Native salt solubilization	2.56
Total	5.54

Compositions of salts vary throughout the San Joaquin Valley. After analyzing salts collected from seven evaporation ponds, Tanji, et al. (1992) found sulfates dominant in the central regions of the valley (Fresno and northern Kings counties), and chlorides prevalent along the southern portion of the Tulare lake bed. Compositions of salt samples collected from evaporation pond basins and IFDM system solar evaporators (Cervinka, 2000) are displayed in Figure 3 with mean concentrations given in Table 2a. Major elements include Na, Ca, Mg, S, and Cl. These samples also include rather large fractions of other materials, mostly due to contamination from soil, many insoluble. Normalized compositions for the samples obtained from the total determined fractions are listed in Table 2b. The normalized concentrations show higher chloride concentrations among samples collected within the Tulare Lake basin (TL, WL) and at the RR solar evaporator site. A sample (ME) collected from another solar evaporator also exhibits a moderately high mean chloride level. Low values of the Na/SO₄ weight ratios (stoichiometric = 0.48) mostly indicate samples with high Ca concentration. One sample (TL) yields a higher concentration of NaCl. In all samples, sulfate dominates, and in particular, sodium sulfate.

Table 2a. Mean compositions of salt samples by location, San Joaquin Valley, California.

Location	(wt. %)					(mg/kg)				(wt. %)	
	Na	Ca	Mg	Cl	SO ₄	K	B	NO ₃	Se	Total	Und.*
LH (6) **	23.78	2.29	0.15	2.72	54.10	863	358	30	4	83.17	16.83
RR (7)	7.64	5.60	0.40	4.93	22.09	849	563	7,030	28	41.51	58.49
TL (6)	27.42	0.21	1.35	7.90	49.12	1,080	111	14	1	86.11	13.89
WL (4)	14.50	2.65	1.95	3.89	36.10	690	267	25	1	59.18	40.82
AA (5)	19.20	2.15	0.78	0.88	46.40	430	465	86	5	69.51	30.49
ME (32)	15.36	4.37	1.55	3.89	37.41	-	634	1,824	8	62.83	37.17
Mean (60)	17.98	2.88	1.03	4.03	40.87	782	400	1,502	8	67.05	32.94
σ	7.07	1.88	0.70	2.35	11.50	241	194	2,801	10	16.50	16.50

Und. = undetermined. ** number of samples from each site in parentheses.

Table 2b. Normalized mean concentrations* of salts and Na to SO₄ weight ratios**.

Location	(wt. %)					(mg/kg)				Na/SO ₄
	Na	Ca	Mg	Cl	SO ₄	K	B	NO ₃	Se	
LH	28.60	2.75	0.18	3.27	65.05	1,037	430	36	5	0.44
RR	18.42	13.48	0.97	11.88	53.21	2,045	1,355	16,937	68	0.35
TL	31.84	0.24	1.56	9.18	57.04	1,254	129	16	1	0.56
WL	24.50	4.47	3.30	6.56	61.00	1,166	452	42	1	0.40
AA	27.62	3.09	1.13	1.26	66.76	619	670	124	7	0.41
ME	24.44	6.96	2.47	6.19	59.54	-	1,009	2,904	13	0.41
Mean	25.90	5.17	1.60	6.39	60.43	1,020	674	3,343	16	0.43

*totals = 100%. **Na₂SO₄ stoichiometric ratio = 0.48.

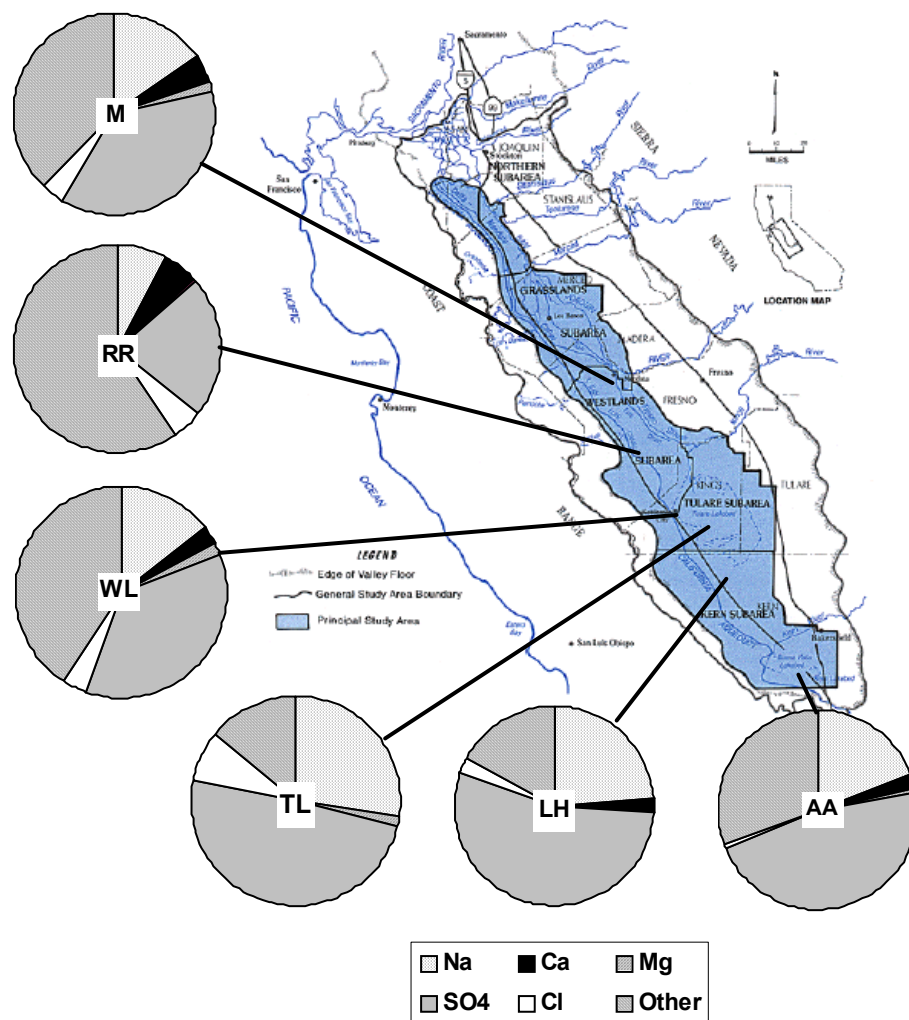


Figure 3. Element concentrations (weight fractions for Na, Ca, Mg, SO₄, Cl, and Other, clockwise from top) for samples collected at six sites along the western San Joaquin Valley. Letters at center of circle charts indicate site from which samples were collected. Shaded area represents land impacted by shallow ground water and saline soils.

Sodium sulfate separation and purification concepts

The IFDM system and the large fraction of sodium sulfate in agricultural drainage salts provide opportunities to recover one or more marketable products including purified sodium sulfate, reclaimed water, and possibly other salts and minerals such as sodium chloride (NaCl). The separation and purification of sodium sulfate from agricultural brines by selective crystallization was suggested by Sun (1997, 1999) following commercial process concepts for sulfate production from natural and other sources. Techniques employing solar concentration and ambient cooling are currently under development as noted later. The solubility characteristics of sodium sulfate are sufficiently distinct from those of the other primary soluble component (NaCl) to allow selective precipitation and removal of the sulfate at purities adequate for some industrial markets.

The basis for the solar salt separation processes under development is the fractional crystallization of sodium-sulfate decahydrate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, mirabilite or Glauber's salt) from solution due to the distinctive solubility characteristic of this compound (Figure 4). This same fractional crystallization is standard industrial practice for the commercial production of sodium-sulfate (Na_2SO_4 , thenardite), although the industrial process typically employs substantial energy input for cooling (Jenkins, et al., 1998). The decahydrate solubility increases steeply with temperature. The concentration in a pure liquid solution in equilibrium with the solid decahydrate increases from 6 g per 100 g pure water (ghg) at 0°C to 55 ghg at 32.4°C . At the latter temperature, the decahydrate solubility becomes equal to the anhydrous sodium sulfate solubility. Whereas the decahydrate solubility increases with increasing temperature, solubility decreases with increasing temperature for solutions in equilibrium with the anhydrous solid. The anhydrous sulfate is unstable at temperatures below the transition temperature of 32.4°C and will crystallize as decahydrate if solid decahydrate is introduced (e.g. as seed crystal) or is otherwise present. The rejection of other ions during sodium sulfate crystallization is high, so good purity can generally be obtained in mixed salt systems.

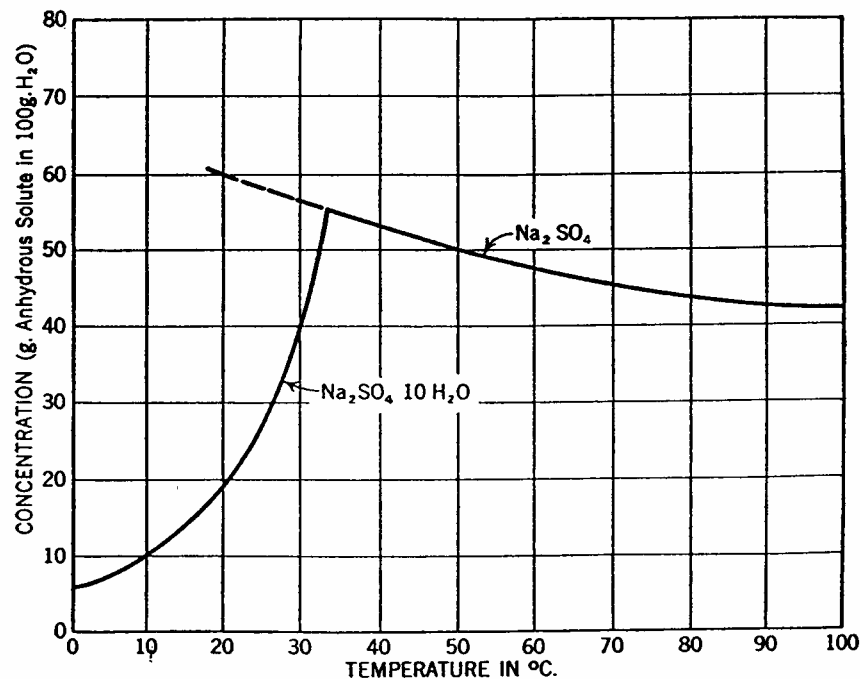


Figure 4. Solubilities (g solute in 100 g water) of sodium-sulfate and sodium-sulfate decahydrate (Cheremisinoff, 1995).

To separate purified sodium sulfate, the salt solution can be concentrated at elevated temperatures and then cooled to precipitate the decahydrate (mirabilite), leaving other salts and impurities in solution. Further melting and drying of the separated decahydrate produces sodium sulfate as a marketable product. The principal means currently under investigation of removing water to concentrate the solution is solar evaporation using either stills to recover distilled water along with salt or open type evaporators to enhance

mass transfer and reduce area required for the concentration system but without distillate recovery. The performance of a horizontal solar evaporator is described by Kim, et al. (2003), and other higher rate designs are also being tested. Other sources of heat, including waste heat, and integrated approaches coupled with reverse osmosis (RO) and other pre-concentration systems can also be used. The separation process is schematically illustrated in Figure 5.

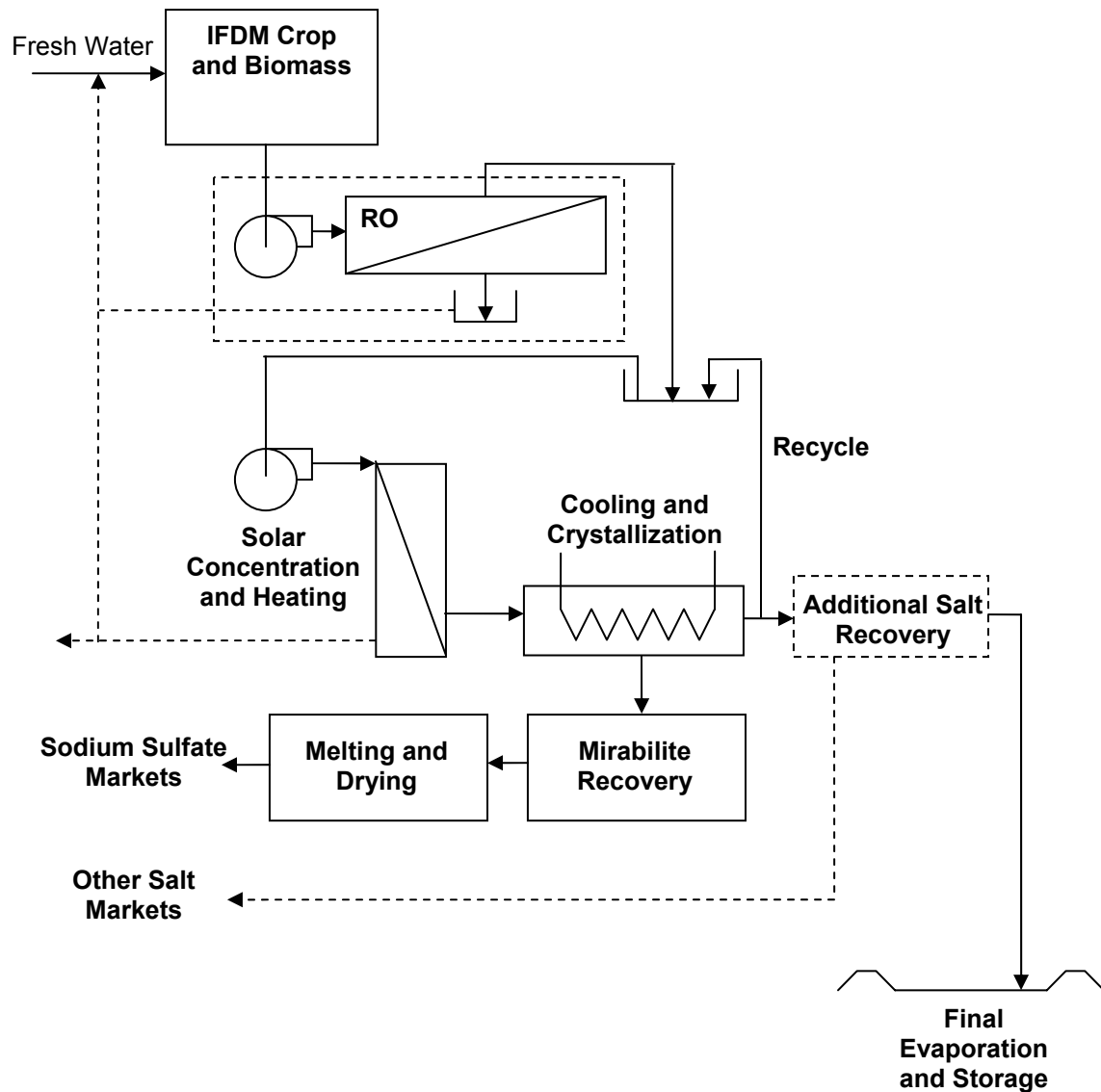


Figure 5. Conceptual salt separation and purification process. The inclusion of a reverse osmosis (RO) or other pre-concentration steps is shown as optional as is the recovery of other purified salts such as NaCl. Waste heat and other energy sources can be used for concentration in substitution of or in combination with the solar process indicated.

Yield of sodium sulfate depends on the concentration in solution and the lowest temperature achievable upon cooling. The theoretical mass yield per unit original mass of water in solution, Y (g g⁻¹), is:

$$Y = \frac{c_f - c_o}{c_f \frac{10W_{H_2O}}{W_{Na_2SO_4}} - 1} \quad [1]$$

where c_f = solubility of sodium sulfate in the cooled solution (g g⁻¹)
 c_o = solubility of sodium sulfate in the concentrated solution (g g⁻¹)
 W_{H_2O} = molar mass of water (g mol⁻¹)
 $W_{Na_2SO_4}$ = molar mass of sodium sulfate (g mol⁻¹)

Concentration to $c_o = 0.40$ g g⁻¹ at 60°C, for example, followed by ambient cooling to 15°C ($c_f = 0.15$ g g⁻¹) should theoretically yield 0.31 g Na₂SO₄ g⁻¹ original water in solution, or 78% recovery. Equation [1] accounts for the water of hydration drawn from solution in crystallizing the decahydrate form that leaves less water in the remaining solution if makeup water is not added to compensate. The water of hydration is later separated during melting and drying of sodium sulfate.

Final yield and purity also depend on the composition of the concentrated solution. As noted earlier, agricultural drainage waters include mixed salts and the potential exists for co-precipitation or co-crystallization of salts (Khamiskii, 1969). Magnesium and potassium ions in particular can co-crystallize with sodium in the formation of sulfate, chloride, and carbonate containing double salts such as astrakhanite (Na₂SO₄.MgSO₄.4H₂O), loeweite (6Na₂SO₄.7MgSO₄.12H₂O), d'ansite (9Na₂SO₄.MgSO₄.3NaCl), vanthoffite (3Na₂SO₄.MgSO₄), and hanksite (KCl.2Na₂CO₃.9Na₂SO₄). In preliminary experiments using prototype solar concentrators and a single ambient-cooled crystallization step, sodium sulfate purities above 94% have been obtained with magnesium constituting the primary contaminant (Kim, et al., 2003). Laboratory purities after single crystallizations tend to be higher, suggesting improvements are possible for field applications. Multiple crystallizations further improve purities (Jung and Sun, 2001). Figure 6 contrasts the concentrations of the major elements and species SO₄, Cl, Ca, and Mg with sodium concentration for the salt samples of Figure 3 collected from throughout the valley. The line SO₄ = 2.089Na is the stoichiometric yield for sulfate in Na₂SO₄ as a function of sodium concentration. The actual sulfate concentrations exceed the stoichiometric values as the concentration of sodium declines. The difference is due principally to increasing calcium concentration indicating the presence of calcium sulfate, although the latter is mostly insoluble at these conditions. The two vertical lines on the graph indicate the stoichiometric fractions of sodium in Na₂SO₄ and NaCl. That sulfate dominates the salt compositions is apparent in the absence of sodium concentrations beyond the Na₂SO₄ limit. There are no specific trends in Cl and Mg concentrations in the samples, although the higher Cl concentrations are observed in several samples with higher Na concentration.

Sodium sulfate recovery can reduce the total quantity of residual salt needing final storage. The residual fraction depends in part on the composition of the drainage water supplied to the concentration system. Table 3 lists predicted species concentrations and masses in concentrate following solar evaporation, residual solution following precipitation of sodium sulfate, and the residual salt evaporite following final evaporation of water as in the system of Figure 5. In this case the precipitate is assumed to crystallize as pure mirabilite (the composition is given for the thenardite form), although in practice magnesium, chloride, and other elements including Se would also likely be present in small amounts. The mass quantities are computed on the basis of actual salt concentrations and water flows at one farm (RR, Cervinka, et al., 1999). Total annual applied fresh irrigation water was 1600 ML (1296 acre-feet) with a total dissolved solids (TDS) concentration of 400 mg kg^{-1} yielding 640 Mg of applied salt. The total drainage water from the halophytes feeding the salt concentration and separation system was 44 ML with a salt concentration of $10,620 \text{ mg kg}^{-1}$ and containing 468 Mg of salt. Some of the applied salt is transported into ground water or is accumulated in biomass. Salt in drainage from the halophytes includes some amount solubilized from soil or applied in fertilizers. Sodium sulfate is assumed to be precipitated at 15°C following brine concentration to 50% salt. The production of sodium sulfate is 129 Mg, leaving 339 Mg of residual solids for other use or disposal. For this site, the composition analyzed and shown in the table accounts for only 75% of the influent solids, the rest being in other

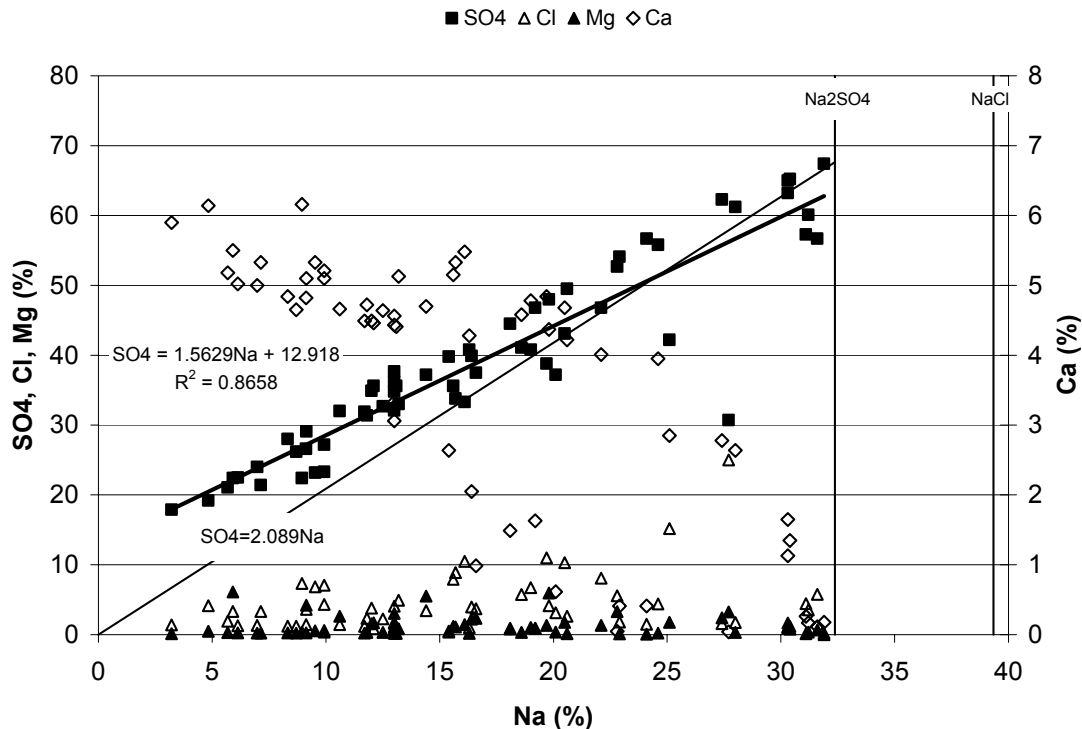


Figure 6. Concentrations of sulfate, chloride, magnesium, and calcium with sodium concentration for drainage salt samples from the San Joaquin Valley.

ions (e.g. carbonate) and contaminants (e.g. insoluble soil solids) that could either be separated prior to concentration or left in the residual fraction. For this starting composition, sulfate recovery is only 28% of total salt. Crystallizing at 15°C recovers 60% of sodium and sulfate from solution. Of some concern is the potentially high concentration of Se in residual salt if not extracted elsewhere in the system. For the example shown in Table 3, the high Se starting concentration in the influent liquid results in an estimated concentration exceeding 100 mg kg⁻¹ in the residual salt. This would be sufficient to classify the residue as a hazardous waste under California regulations (total threshold limit concentration, TTLC = 100 mg kg⁻¹, 22CCR66261.24(a)(2)¹) although this is not a generally anticipated result and some Se will occur in the separated sodium sulfate and some will volatilize during concentration.

Table 3. Projected concentrations and salt masses, RR site data.

Concentration (mg kg ⁻¹)					
	Influent	Concentrate	Precipitate	Residual	Residual Evaporite
Total Salt	10,620	500,000	1,000,000	526,978	1,000,000
NO ₃ -N	70	3,296		4,802	9,113
Cl	2,226	104,802		152,718	289,800
SO ₄	2,686	126,460	676,056	47,968	91,026
Na	2,207	103,908	323,944	86,100	163,384
Ca	629	29,614		43,153	81,889
Mg	162	7,627		11,114	21,091
B	17	800		1,166	2,213
Se	0.8	37		54	103
Reconstructed	7,998	376,544	1,000,000	347,077	658,618
Fraction of Total (%)	75.3	75.3	100	65.9	65.9

Mass (Mg y ⁻¹)					
Total Salt	468.0	468.0	129.5	338.5	338.5
NO ₃ -N	3.1	3.1		3.1	3.1
Cl	98.1	98.1		98.1	98.1
SO ₄	118.4	118.4	87.5	30.8	30.8
Na	97.3	97.3	42.0	55.3	55.3
Ca	27.7	27.7		27.7	27.7
Mg	7.1	7.1		7.1	7.1
B	0.7	0.7		0.7	0.7
Se	0.03	0.03		0.03	0.03
Reconstructed	352.4	352.4	129.5	222.9	222.9
Fraction of Total (%)	75.3	75.3	100	65.9	65.9

The site specific dependence of the residual concentrations is indicated by the alternative composition of Table 4. In this case, the influent concentrations have been determined from the normalized salt composition of site AA as no specific influent water analyses are available. Masses are based on the same water flows of the RR site analyzed above. The relatively high sodium sulfate concentration at this site leads to a lower residue mass

¹ Title 22, California Code of Regulations, Division 4.5, Chapter 11, Article 3, Section 66261.24.

that is 15% of initial salt. Sulfate recovery might be as high as 90%. The lower starting Se concentration results in a final residue concentration about half the California TTLC.

Table 4. Projected concentrations and salt masses, AA site salt composition.
Concentrations (mg/kg)

	Influent	Concentrate	Precipitate	Residual	Residual Evaporite
Total Salt	10,620	334,000	1,000,000	139,933	1,000,000
NO3-N	1	41		117	833
Cl	134	4,208		11,842	84,624
SO4	7,096	223,178	676,056	87,218	623,285
Na	2,933	92,251	323,944	460	3,289
Ca	328	10,321		29,040	207,530
Mg	120	3,774		10,620	75,893
B	7	224		630	4,500
Se	0.1	2		7	47
Reconstructed	10,620	334,000	1,000,000	139,933	1,000,000
Fraction of Total (%)	100.0	100.0	100	100.0	100.0

Masses (Mg)					
Total Salt	468.0	468.0	398.3	69.7	69.7
NO3-N	0.1	0.1		0.1	0.1
Cl	5.9	5.9		5.9	5.9
SO4	312.7	312.7	269.3	43.4	43.4
Na	129.3	129.3	129.0	0.2	0.2
Ca	14.5	14.5		14.5	14.5
Mg	5.3	5.3		5.3	5.3
B	0.3	0.3		0.3	0.3
Se	0.003	0.003		0.003	0.003
Reconstructed	468.0	468.0	398.3	69.7	69.7
Fraction of Total (%)	100.0	100.0	100	100.0	100.0

Ambient conditions for solar concentration systems

The performance of the solar concentrator and the crystallizer are heavily dependent on the ambient meteorological conditions. Data for two representative locations (Firebaugh and Five Points, CA) during 2002 are shown in Figures 7 - 13. Data were obtained from the California Irrigation Management Information System (CIMIS)² operated by the California Department of Water Resources. The valley is characterized by hot summers with low average daily humidities. Horizontal solar radiation averages approximately 8 kWh m⁻² d⁻¹ in July with an annual total of 1.8 – 2.0 MWh m⁻²). The west side of the valley is subject to nearly constant winds from the west and north-west in the summer, shifting to the south in the winter. There is virtually no rainfall for four months from May to September, and evapotranspiration (ET_o) remains high with daily rates above 7 mm (7 L m⁻² d⁻¹). Some concentrator designs have achieved well above this but are still undergoing testing and development. Annual ET_o is around 1.5 m. Summer nighttime

² <http://www.cimis.water.ca.gov/> Complete 2002 precipitation and ET_o data not available for Five Points.

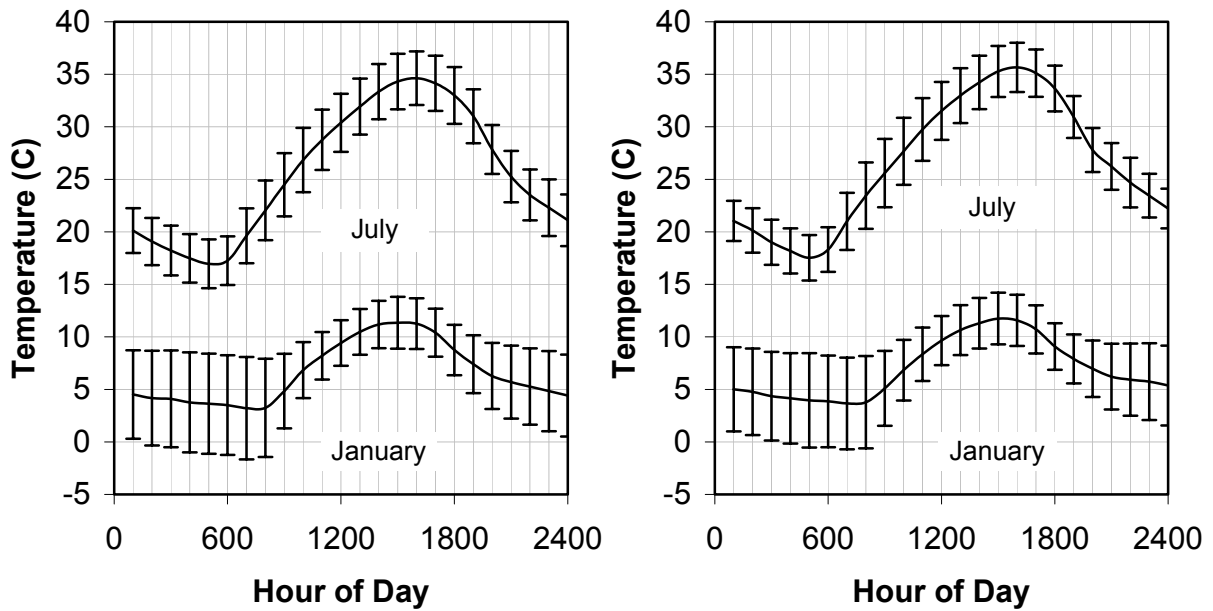


Figure 7. Mean air temperatures (°C) for Firebaugh (left) and Five Points (right), California, January and July 2002. Error bars are \pm one standard deviation. Hour of day is Pacific Standard Time (PST).

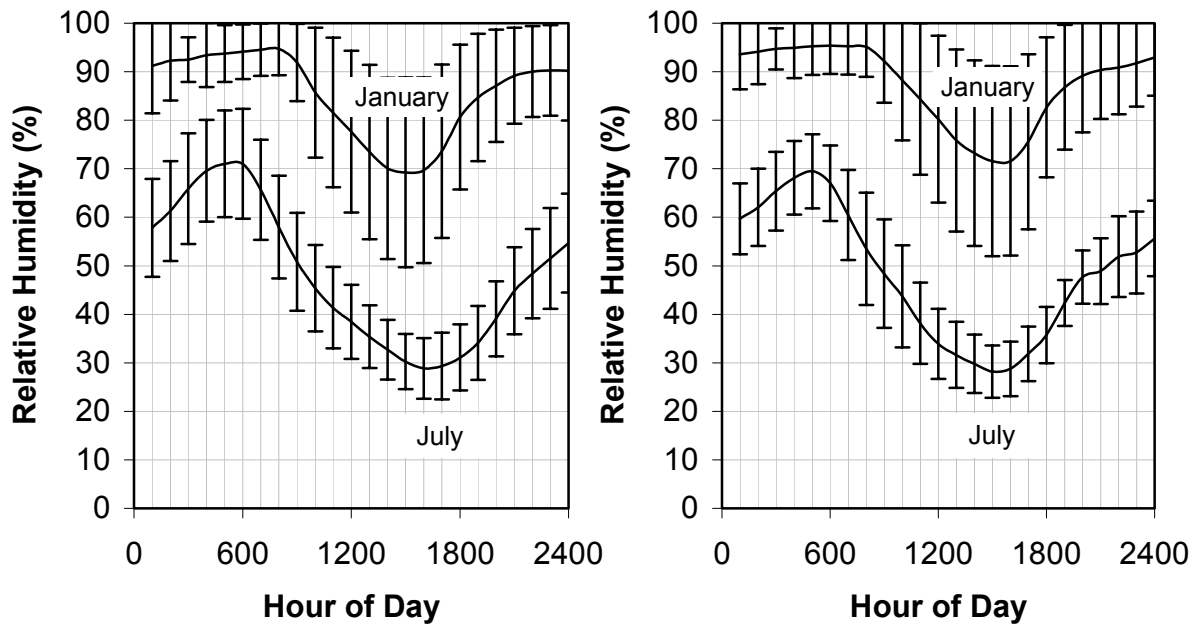


Figure 8. Mean relative humidity (%) for Firebaugh (left) and Five Points (right), California, January and July 2002. Error bars are \pm one standard deviation.

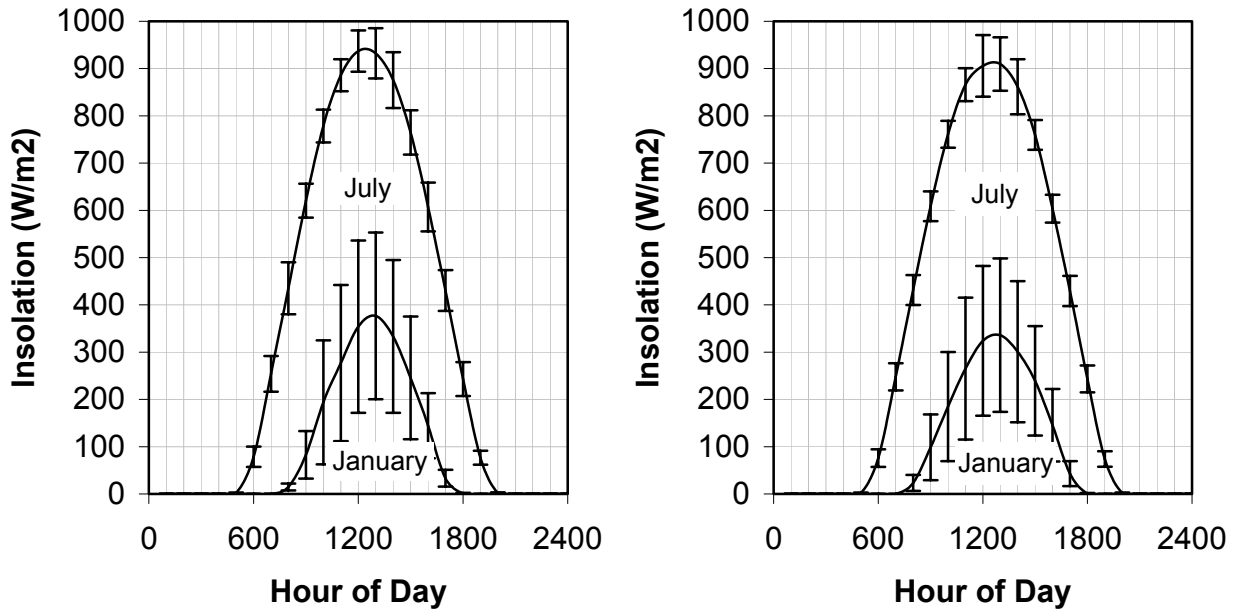


Figure 9. Mean global horizontal solar radiation (W m^{-2}) for Firebaugh (left) and Five Points (right), California, January and July 2002. Error bars are \pm one standard deviation. Mean daily energy for Firebaugh is 2.1 kWh m^{-2} in January, 7.9 kWh m^{-2} in July. Mean daily energy for Five Points is 2.0 kWh m^{-2} in January, 7.8 kWh m^{-2} in July.

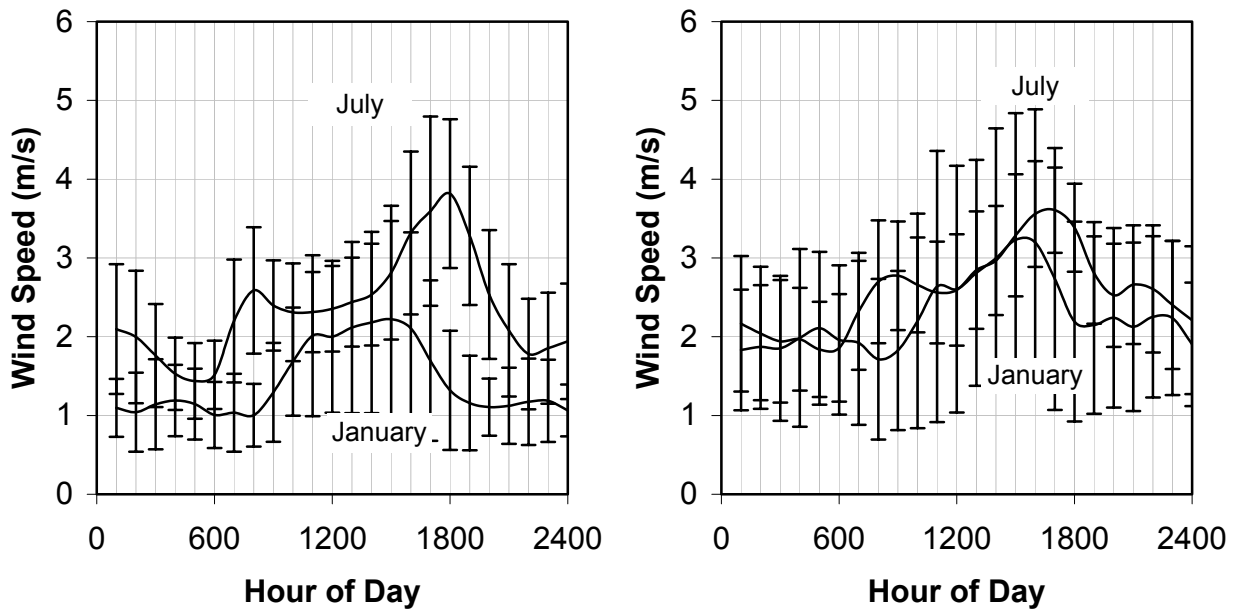


Figure 10. Mean wind speed (m s^{-1}) at 2 m for Firebaugh (left) and Five Points (right), California, January and July 2002. Error bars are \pm one standard deviation.

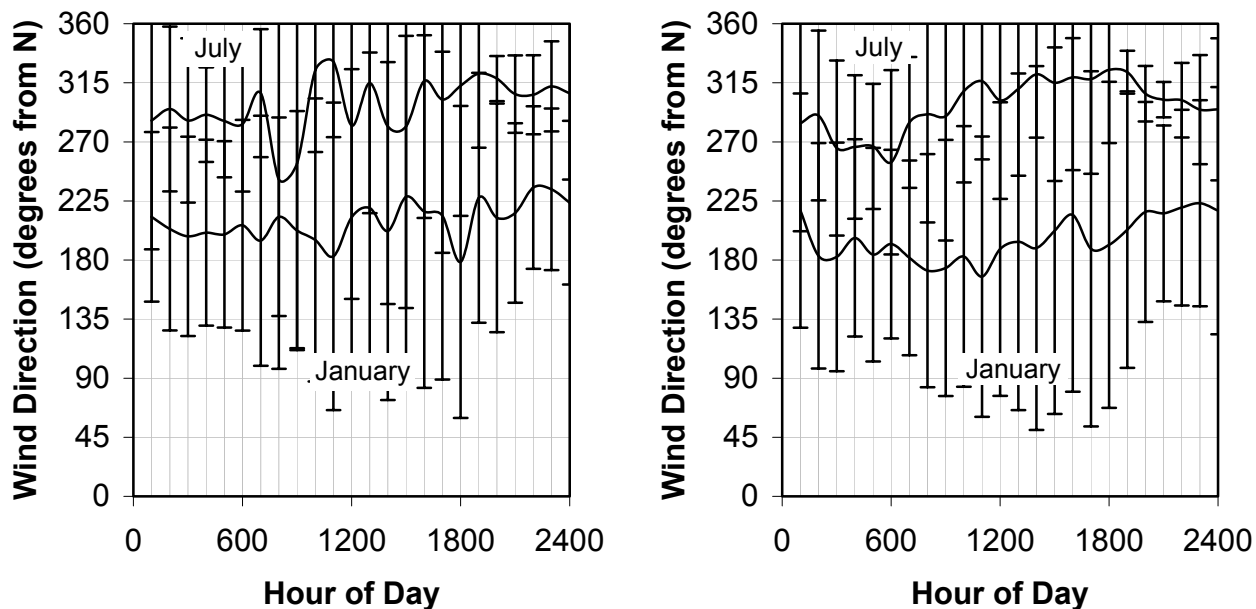


Figure 11. Mean wind direction (degrees from North) at 2 m for Firebaugh (left) and Five Points (right), California, January and July 2002. Error bars are \pm one standard deviation.

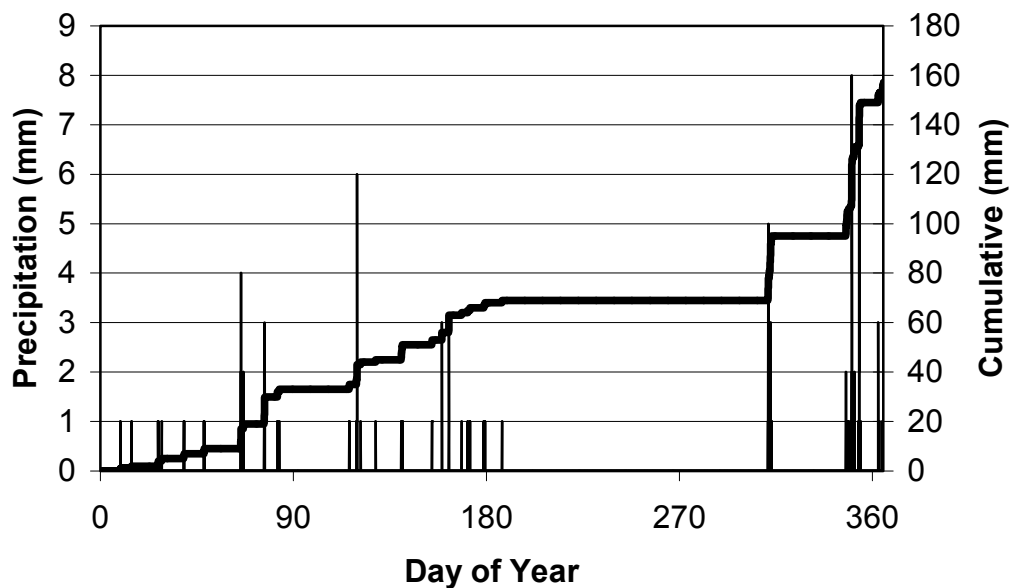


Figure 12. Precipitation for Firebaugh, California, 2002.

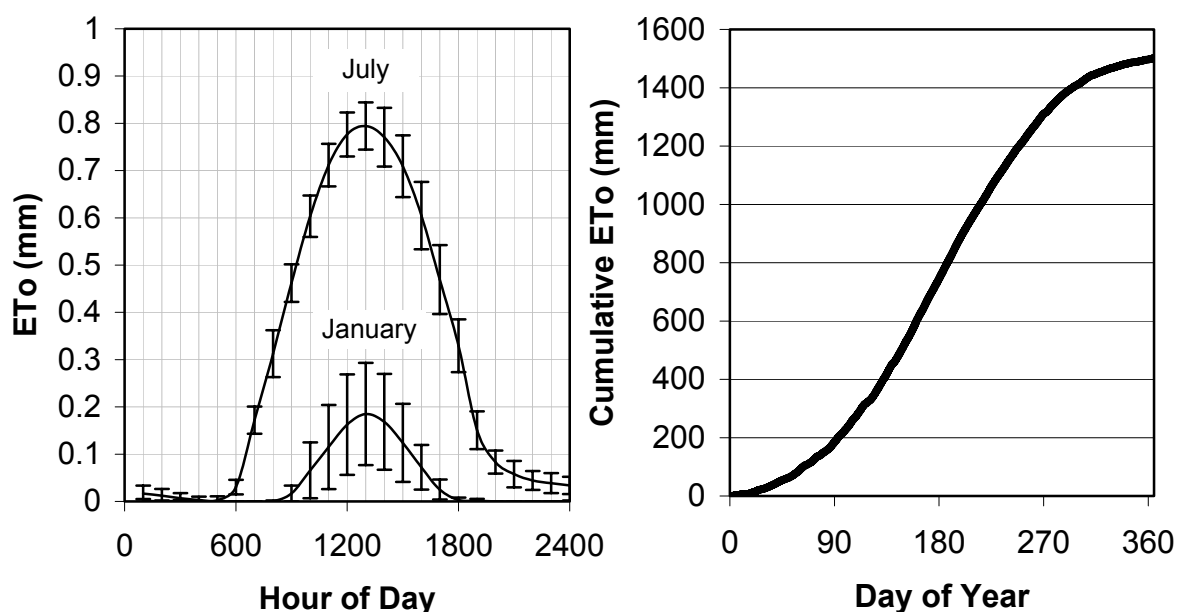


Figure 13. Mean hourly evapotranspiration ETo (left) and cumulative evapotranspiration (right) for Firebaugh, California, 2002. Error bars are \pm one standard deviation. Mean daily ETo is 0.9 mm in January, 7.2 mm in July.

air temperatures seldom decline below 15°C, but clear skies allow for radiative cooling to assist in achieving lower temperatures for sulfate crystallization. The lower wintertime temperatures suggest the possibility of storing brine concentrated during the summer for crystallization during the winter, with residue evaporite and dehydrated sodium sulfate (if not handled otherwise) produced the succeeding summer in an annual cycle. Similar strategies have been suggested for use with salt-gradient solar ponds that might also recover heat and power.

Sodium sulfate markets and purity requirements

Sodium sulfate is used in several markets but is not a major commodity chemical. Principal markets are in detergents, textile dyeing, pulp and paper, and glassmaking. Current US production (0.5 Tg y^{-1}) of natural and synthetic sodium sulfate is roughly 10% of world (5.2 Tg y^{-1} ; Kostick, 2003). By comparison, US and world sodium chloride production is 44 and 225 Tg y^{-1} , respectively. US production of sodium sulfate has remained relatively constant over the last decade while annual imports and exports have fluctuated from below 0.1 Tg to more than 0.2 Tg (Figure 14). Domestic production of natural sodium sulfate is by only two producers in California and Texas. Apparent US consumption has been consistently declining since peaking in 1973. The value of sodium

sulfate increased rapidly from 1973 to 1983 and has remained relatively stable since then at around \$90 Mg⁻¹. In real value sodium sulfate has not changed much over the last 80 years (Figure 14). For the case of the RR site, the recovery of 129 Mg y⁻¹ would provide roughly \$12,000 additional revenue if sulfate were marketed at average unit value. This amounts to about \$45 ha⁻¹ y⁻¹ of total land generating the drainage for salt recovery (259 ha), but more than \$2,200 ha⁻¹ y⁻¹ based on the 5 ha required to evaporate 44 ML over 120 days at an average evaporation rate of 7 L m⁻² d⁻¹. With enhanced evaporation rates demonstrated by more sophisticated systems, revenues might increase above \$4,500 ha⁻¹ y⁻¹ while reducing area required. With higher purity feed, recovery of up to 400 Mg y⁻¹ of sodium sulfate would yield \$36,000 additional revenue and up to \$14,000 ha⁻¹ y⁻¹ based on the land area for high rate systems. Full capital and operating costs are not yet known for these systems meeting environmental compliance and economic feasibility remains uncertain. The actual market value for agricultural drainage derived salt also remains uncertain until routine purities and marketing options can be established.

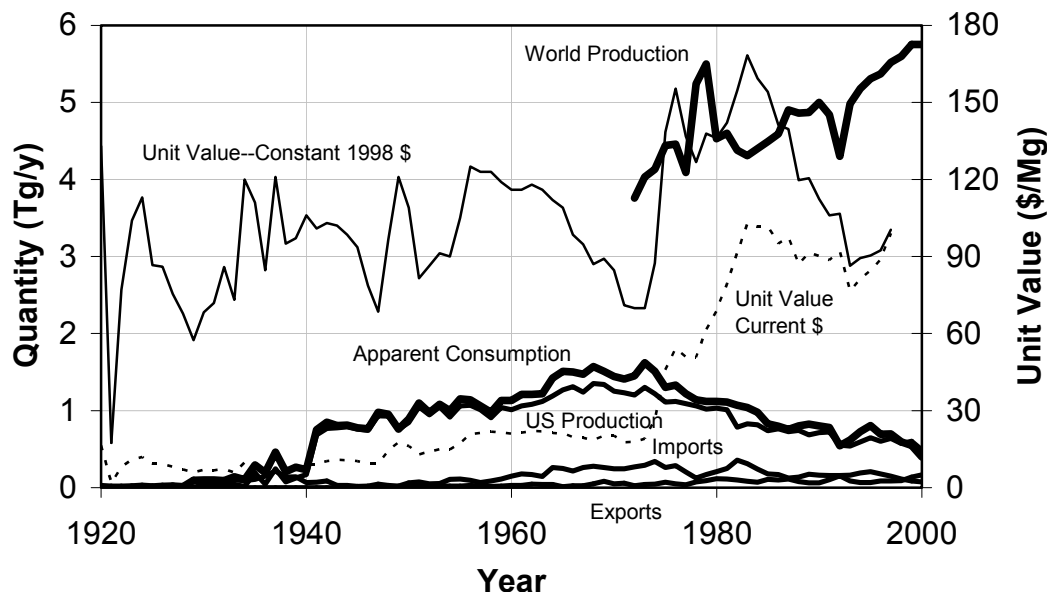


Figure 14. Production and value of commercial sodium sulfate (Kostick, 2003).

Approximately 80% of world sodium sulfate production is used in detergents and growth in powdered detergent sales outside the US has caused US exports to increase recently. Increasing imports of textiles from overseas has led to reduced manufacturing and decreased demand for sodium sulfate in textiles in the US. The use of salt from the ME and RR sites has been explored for textile dyeing, with good results as long as sodium sulfate purity is kept high, generally above 99% (Jung and Sun, 2001). Crude salts are not likely to satisfy the demands of this market.

The primary use of sodium sulfate in glassmaking is as a fining agent to expel bubbles in the melt via flotation (Jenkins, et al., 1998). Its use in this regard is generally constrained to less than 1 wt %, and a number of other compounds can substitute although they are not generally as effective. The use of sodium sulfate in place of sodium carbonate as a

source of sodium oxide in soda-lime glass would greatly expand the market, but the decomposition of sulfate leads to large emission of SO_2 needing control, adding to the cost of glass manufacturing. Furnace corrosion rates are higher when using sulfate. Experimental glasses have been produced using crude agricultural drainage salt recovered from one site (ME) containing 94-99% sodium sulfate. Sample glasses were made from salt and analytical grade silica as well as silica from rice straw, a high silica biomass (Figure 15). Work is continuing on the possible use of salt in glass, ceramics, and other materials. Industrial purity specifications for glassmaking are also high, usually greater than 99% (Table 5).

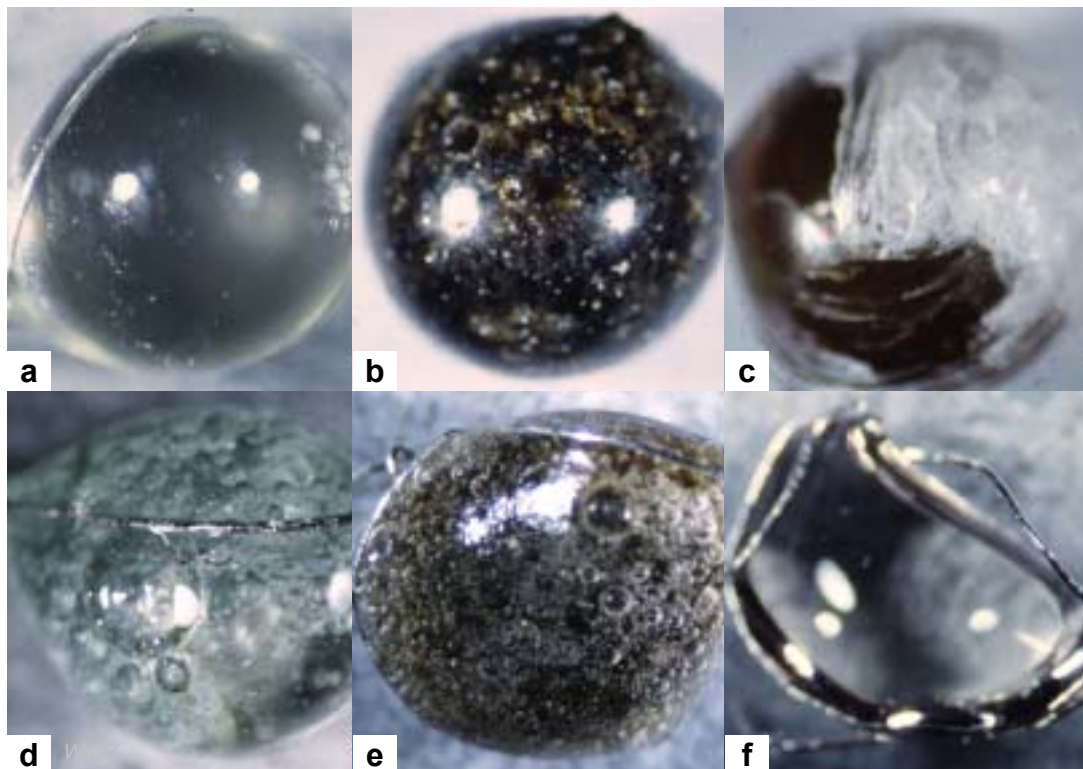


Figure 15. Glasses produced from solar evaporator salt (site ME) and various sources of silica. (a) soda-lime glass from mixture of 33.7 wt. % salt, 21.2% calcium carbonate, and 73.8% silica, 1255°C. (b) 15% salt in unleached rice straw ash, 1055°C. (c) 30% salt in unleached rice straw ash, 1055°C (sulfate precipitation visible on surface). (d) 16.2% salt in leached rice straw ash, 1305°C. (e) hydrated unleached rice straw ash only, 1117°C. (f) 30% salt in hydrated mixture with unleached rice straw ash, 1099°C. Platinum support wires visible in (a), (d – f) (after Jenkins, et al., 1998).

Separate recovery of sodium chloride could address a wide number of commercial markets. Calcium chloride and magnesium chloride, along with sodium chloride, are used as chemical suppressants in road deicing and dust control. While recovery of sodium chloride from agricultural drainage would not likely have a marked impact on global salt markets, recovery of sodium sulfate could. Although there is some uncertainty as to the total quantity of salt needing recovery or disposal for proper salinity

management, with approximately 80% of the agricultural drainage salt in the San Joaquin valley present as sodium sulfate the recovery of even a relatively small fraction could have a substantial impact on the US and foreign markets. Development of other markets and uses for sulfate may be needed for large scale application of salt recovery systems.

Table 5. Compositions and specifications (wt %) of commercial sodium sulfates for glass making (Jenkins, et al., 1998).

Compound	Source 1 ^a	2 ^a	3 ^a	4 ^b	5 ^b	6 ^b	7 ^b	8 ^b
Na ₂ SO ₄				>99.45	>99.5	>99.3	>98.5	>99.5
Na ₂ O	43.45	43.55	43.55					
Na ₂ CO ₃	0.10						<0.3	
NaCl						<0.5	<0.5	<0.25
SO ₃	56.10	56.7	56.30					
SiO ₂								
Cl	0.002	0.012	<0.001	<0.20				
Fe ₂ O ₃	0.0017	0.0008	0.00035			<0.001		
Fe								<0.002
CaO	(<0.04) ^c	(<0.04)	(<0.04)					
MgO								
Al ₂ O ₃	(<0.006)	(<0.006)	(<0.006)					
TiO ₂	(<0.005)	(<0.002)	(<0.002)					
CO ₂								
K ₂ O								
P ₂ O ₅								
As ₂ O ₃	(<0.005)	(<0.13)	<0.0003					
ZnO	(<0.005)		0.00012					
NiO	(<0.005)	(<0.004)	0.00130					
Ni				<0.001	<0.001	<0.001	<0.001	
Cr ₂ O ₃	(<0.005)	(<0.0015)	0.00060					
Heavy metals (Pb)	(<0.005)	(<0.0011)	<0.001					
Se	(ND)	(ND)	<0.003					
Moisture				<0.20	<0.1	<0.25		
Loss on Ignition	0.17	0.10	0.10					
Insolubles	0.01	0.03		<0.05	<0.1		<1.0	

^aactual composition. ^bproduct specification. ^cparentheses indicate semi-quantitative analysis (ND = not detected).

Summary and Conclusions

Agriculture on the west side of the San Joaquin Valley of California, like many irrigated arid land agricultures, suffers from increasing soil salinity and faces large scale land retirement in the near future if salts cannot be removed. Integrated farm drainage management (IFDM) systems employing sequential water reuse have emerged in recent years as potential phytoremediation techniques to improve salinity management. Solubility characteristics of sodium sulfate offer the potential to recover purified sulfate for commercial markets. Salt separation and purification using solar concentration and ambient cooling processes are currently being analyzed and tested. Sodium sulfate recoveries depend on the composition of the drainage feed to the concentrator along with local meteorological conditions and may range from as low as 28% to more than 85% of total salt. Purities from preliminary experiments employing single crystallization steps following concentration and ambient cooling remain below most industrial specifications, and further development is needed to determine if adequate purity can be achieved.

Acknowledgements

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Unit Conversions

SI unit	Multiply by to obtain	Conventional unit
ha	0.4047	acre
Mg (t, 10^6 g)	1.1023	short ton (2000 lbs)
Tg (10^{12} g)	1.1023	million short tons
m	3.2808	ft
km ³	0.8107	million acre-feet